Applied Surface Science 331 (2015) 392–398

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Efficient localized heating of silver nanoparticles by low-fluence femtosecond laser pulses

H. Huang[a,b], M. Sivayoganathan[a,b], W.W. Duley[a,c], Y. Zhou[a,b,*]

[a] Centre for Advanced Materials Joining, University of Waterloo, Ontario, N2L 3G1, Canada
[b] Department of Mechanical & Mechatronics Engineering, University of Waterloo, Ontario, N2L 3G1, Canada
[c] Department of Physics & Astronomy, University of Waterloo, Ontario, N2L 3G1, Canada

ARTICLE INFO

Article history:
Received 20 September 2014
Received in revised form
22 December 2014
Accepted 12 January 2015
Available online 20 January 2015

Keywords:
Femtosecond laser
Localized heating
Localized surface plasmon

ABSTRACT

Highly localized heating can be obtained in plasmonic nanomaterials using laser excitation but the high fluences required often produce unacceptable damage in and near irradiated components and structures. In this work we show that plasmonic nanostructures involving aggregated Ag nanoparticles (Ag NPs) can be heated effectively without attendant damage to the surrounding material when these structures are irradiated with many overlapping femtosecond (fs) laser pulses at very low fluence. Under these conditions, the effectiveness of heating is such that the temperature of 50 nm Ag NPs can be raised to their melting point from room temperature. Aggregates of these NPs are then observed to grow into larger spherical particles as laser heating continues. Imaging of these materials shows that the initiation of melting in individual Ag NPs depends on the local geometry surrounding each NP and on the polarization of the incident laser radiation. Finite difference time domain (FDTD) simulations indicate that melting is triggered by localized surface plasmon (LSP)-induced electric field enhancement at "hotspots".

1. Introduction

The control of localized heating on micro- and nanoscales is emerging as a powerful way of manipulating thermally activated processes in medical therapy [1], ultrafast switching of phase-change materials [2], nanowelding [3], and nanoscale chemical interactions [4]. Realization of nanoscale thermal control usually involves the assembly of a nanoscale electro-thermal system consisting of nanowire or nanotubes [3,4]. Currently, this can only be accomplished using expensive and sophisticated devices such as thermal cantilevers, the atomic-force microscope and scanning electron microscopy (SEM). Laser radiation can also be used for nanoscale heating but this requires complex optical systems to achieve the spatial resolution necessary for nanoscale processing [5,6].

Recently, plasmonic nanomaterials or structures have been reported to produce highly localized heat generation under laser irradiation [7–10]. The heating in plasmonic nanomaterials and structures is mainly attributed to the concentration of laser energy in hotspots where the electric field is enhanced due to localized surface plasmon (LSP) [9,10]. Because the hotspots are localized near the surface of these materials, nanoscale heating utilizing plasmonic nanomaterials and nanostructures is promising. In addition as the generation of hotspots, including the location and amplitude of the electric field enhancement factor, depends on structure geometry together with laser polarization [11,12], the nanoscale laser heating process can be influenced through control of these parameters.

Due to the high intensity in fs laser pulses and their short duration which minimizes heat conduction compared to longer pulse lasers, fs laser irradiation is an efficient way to direct energy to hotspots in plasmonic nanomaterials [13]. In this paper, we show that fs laser irradiation with fluence as low as ~7.2 mJ/cm^2 is effective in the localized heating and melting of individual Ag NPs contained in extended plasmonic nanostructures. This fluence is much lower than that previously reported (~110 mJ/cm^2) for fs laser irradiation induced melting of Ag nanomaterials [9]. Under these irradiation conditions, there is no apparent damage to Ag NPs surrounding the selected plasmonic structure.

2. Experimental and simulation

Ag NPs with a ~2 nm thick PVP coating were prepared following the method reported by Peng et al. [14]. Sodium citrate

* Corresponding author: Centre for Advanced Materials Joining, Department of Mechanical & Mechatronics Engineering, University of Waterloo, Ontario, N2L 3G1, Canada.
E-mail address: nzhou@uwaterloo.ca (Y. Zhou).

http://dx.doi.org/10.1016/j.apsusc.2015.01.086
0169-4332/

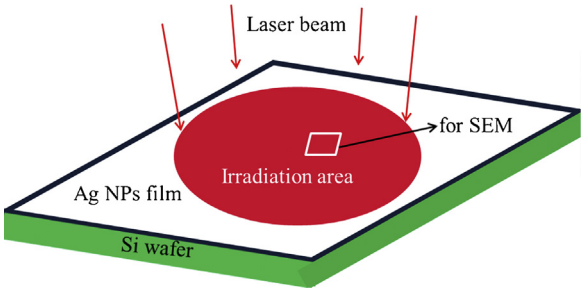

Fig. 1. Schematic of the experimental configuration.

($Na_3C_6H_5O_7$) aqueous solution (12 ml, 200 mM) was added to 200 ml deionized water with vigorous stirring, followed by adding polyvinylpyrrolidone (PVP, 2 ml, 20 mM), $[Ag(NH_3)_2]^+$ (2 ml, 120 mM), and Ag seed (~5 nm diameter, 0.4 ml, 1 mM) aqueous solution. Then ascorbic acid ($C_6H_8O_6$) aqueous solution (10 ml, 10 mM) was added drop-wise and the mixed solution was stirred for 30 min. The prepared Ag NPs solution were then centrifuged and re-dispersed into deionized water to eliminate the residual PVP, Ag seed, and other ions in the solution. Ag NPs films with NPs embedded in the PVP matrix were obtained by immersing clean silicon wafers into the re-dispersed Ag NPs solution and keeping them in a dry environment (humidity ≤35%) to let the water evaporate. Ag NPs films on silica glass were also prepared using a similar method and then used for UV–vis absorption spectroscopic investigation.

The Ag NPs films were irradiated for up to 60 s with fs laser pulses (Coherent Inc., wavelength = 800 nm, pulse duration = 35 fs, repetition rate = 1 kHz) at average fluence (calculated by divide the spot area with the pulse energy) ranging from ~3.6 mJ/cm^2 to 28.8 mJ/cm^2. The schematic of the experimental setup is shown in Fig. 1. The morphology of the Ag NPs films in the irradiation area before and after laser irradiation was characterized by SEM (LEO 1550) and transmission electron microscopy (TEM, JEOL, JEM-2010F). Commercial finite difference time domain (FDTD) software (Lumerical Inc.) was used to simulate the distribution of hotspots and the absorption in plasmonic Ag NPs structures during irradiation with 800 nm laser light.

3. Results and discussions

The SEM images of Ag NPs film morphology before and after laser irradiation are shown in Fig. 2. Due to the nature of the deposition process, these films had a non-uniform thickness distribution. At their thickest point, the films contained ~6 layers of Ag NPs. Fig. 2a–b shows that, before irradiation, most of the individual NPs in these films had sizes between 20 and 80 nm with an average size of 50 nm. Individual NPs were irregularly shaped as shown in the inset in Fig. 2a. After irradiation for 10 s (10,000 pulses), at a fs laser fluence of ~7.2 mJ/cm^2 some spherical particles were generated, as indicated by the dashed circles in the inset image in Fig. 1c. The size distribution of these newly formed spherical particles, averaged over 300 particles, is given in Fig. 2d. It can be seen that large spherical particles having diameters between 80 and 160 nm appear after 10 s laser irradiation. Particles in this size range were not present before irradiation. The generation of larger spherical particles suggests that fs laser irradiation under these conditions produced efficient heating which caused the melting and subsequent coalescence of the original Ag NPs. Molecular dynamic simulations and experimental observations of the solid-state sintering behavior of NPs [15,16] has shown that sintered NPs will not grow into larger sphere-like structures until the sintering temperature approaches the melting point. No apparent change was observed in either the morphology or size distribution of these generated spherical particles when the irradiation time was increased to 30 and 60 s. As shown in Fig. 3, the size of the large spherical particles is still in the 80–160 nm range after the NP film was irradiated at a fluence of ~7.2 mJ/cm^2 for 30 s (Fig. 3a and b) and 60 s (Fig. 3c and d). This indicates that the generation of spherical particles does not depend on the irradiation time and implies that other factors such as laser fluence and the localized structure in the NP film may dominate the interaction.

Fig. 4 shows SEM images of the morphology in Ag NPs film irradiated at different fluences for 10 s. At 28.8 mJ/cm^2 (Fig. 4a), the NPs in the irradiated film were melted and sintered due to the large energy input, and the Si wafer shows the development of small holes (see the arrows in Fig. 4b). These holes are the result of ablation. Since this fluence is much smaller than the damage threshold in Si (170 mJ/cm^2) irradiated with a 25 fs pulse. [17], hole drilling in the Si wafer can be attributed to an enhancement in the local laser intensity as a result of multiple scattering [18]. At a laser fluence of ~14.4 mJ/cm^2, spherical particles are also obtained and the size distribution of these spherical particles is almost the same as that in samples irradiated at a fluence of ~7.2 mJ/cm^2. The only exception is that a few slightly larger (160–220 nm) particles are also generated (Fig. 4c and d). When the laser fluence was decreased to 3.6 mJ/cm^2 (Fig. 4e), modification was not evident in the irradiated NP films. These observations indicate that the generation of spherical particles is influenced by the laser fluence, but there is no direct correlation between laser fluence and the resulting size of the spherical particles.

Enhancement in the local laser intensity due to multiple scattering, including speckle formation and sub-wavelength self-focusing [18], was first considered as the origin of efficient heat generation leading to the melting of Ag NPs and formation of larger size spherical particles. This might be expected to be important in multiple-layer Ag NP films. For example, sub-wavelength self-focusing of an incident laser beam was observed at the bottom surface of a multiple layer ZnO NP film [18]. The laser intensity in the self-focused beam was enhanced by a factor of 2.5. In the present experiments, the enhancement factor was estimated to be ~6. This value was obtained from the ratio of the fluence (~28.8 mJ/cm^2) consistent with producing visible damage to the Si substrate in the present experiments to that reported as the damage threshold (170 mJ/cm^2) for irradiation of Si with a 25 fs pulse [17]. Based on this comparison, we conclude that sub-wavelength self-focusing is not the primary source of the efficient heating and melting of NPs found in the present experiments [13].

To minimize the influence of sub-wavelength self-focusing, and to investigate the underlying causes of efficient fs laser induced localized heating, single-layer Ag NPs films were prepared and irradiated under the same conditions. Fig. 5 shows SEM images of the morphology of single-layer NPs films before and after 16 laser pulses, which was the minimum number of overlapping pulses needed to produce an observable change in the single layer Ag NP film. These images show that larger spherical NPs can also be generated in single-layer NPs films after fs laser irradiation (as indicated by arrows in Fig. 5b). This implies that multiple scattering induced sub-wavelength self-focusing is not the source of the efficient heating effect resulting in melting of the original NPs. SEM observations in the same area of the NPs film before (Fig. 5a) and after (Fig. 5b) fs laser irradiation show that, a large spherical particle has been created in the structure where 4 NPs were located (ring 1 in Fig. 5a and b). This particle is shown in the inset image in Fig. 5b. Removal of NPs from the PVP matrix leaves and outline of their original positions (e.g. ring 2 in Fig. 5b). The inset image in Fig. 5b indicates that 3 of the 4 adjacent Ag NPs coalesce into a larger particle while the remaining NP was unaffected. This suggests that selective fs laser induced heating of Ag NPs is concentrated in certain